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Protection and Modeling in the Use of S, Ca, and Mg Alternatives for Long-Term Sustainable Fertilization Systems

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Abstract: The complexity of NP and NPK fertilizers in stationary and long-term system yields is proven to determine substantial changes in soil fertility, revealing interaction possibilities related to the chemistry and requirements of other nutrients (S, Ca, Mg, and microelements), while sustainable fertilization can exert control over them through rational fertilization practices and complex nutritive management. Revealing the extent of the modifying effects in the application of S, Ca, and Mg correlated to the soil-plant system conditions relates to the hypothesis of the present research in the context of long-term experiments in Romania at the Office of Pedological and Agrochemical Studies Alba (OSPA Alba) and the Turda Agricultural Research and Development Station (SCDA Turda) with 55 years of a fertilizing effect over the 1967–2022 period, but not solely. This study shows that for sustainable fertilization systems, the complementary application of S, Ca, and Mg with NP and NPK has proven to be effective and unitarily constitutes a measure for the sustainable protection and enhancement of soil fertility.

Keywords: secondary macroelements; nutrient interactions; sustainability

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1. Introduction

In the fields of soil science, nutrition, and fertility, specific studies, particularly in terms of practical fertilization measures, are considered for the optimization of the effective nutrient regime and management. This scientific approach includes organogenic elements—C (45% of plant dry matter), O (42% of dry matter), and H (6.5% of dry matter)—devoid of special application through fertilizers, but also the relevant essential elements for fertilizing interventions, classified as primary macroelements, N (0.2–6% of dry matter), P (0.2–1.7% of dry matter), and K (0.4–6% of dry matter) as well as the secondary macroelements S (0.02–1.3%), Ca (0.01–7%), and Mg (0.1–0.9), which are applied through fertilizers. These secondary ones, by comparison to the primary category, are applied at lower fertilizer rates and under special conditions in the nutrient medium [1–5].

In plant nutrition, these elements are accompanied by trace elements that play an essential role as well, namely Fe, Mn, Cu, Zn, B, Mo, etc., with such plant concentrations that do not exceed 0.01% of s.u. and with a range of representation in plant tissues of n.10-2–n.10-6% of dry matter [4,6–12].

All elements have essential roles in the crop life cycle, and macroelements mainly play plastic, constitutive, and qualitative roles while trace elements have mainly enzymatic and catalytic roles in plant metabolism [4,5,13–16].

Such elements mentioned as S, Ca, and Mg have specific functions and roles, interrelated with other elements (S with N and P, with some cations, and Ca, Mg, and K in dependence on the rest of the cations in CEC or T). On an overall basis, they have had less representation in fertilization. However, in the past 2–3 decades, based on these complex dependencies and changing anthropogenic factors in fertilization, especially in sensitive plant species or in high consumers of these nutrients, they are commonly applied in the background of NPK. Obviously, the specificity of their roles and chemistry in a soil-plant system and their changes and efficiency are different and at times more complicated [4,5,17,18].

In long-term experiments and multi-year fertilization without S inclusion, S chemism undergoes modifications and processes, such as the following:

- With decreasing pH, through acidification, the soil S content decreases by increasing anion adsorption in clay (as SO_4^{2-});
- The organic and mineral S content decreases with the reduction in humus and organic C content through fertilization and conventional technologies;
- Degradation of the soil S regime occurs as a result of excessive NP and NPK fertilization where excess N is the determining factor [19,20].

In the case of calcium, research needs to consider its chemism and effect in a soil-plant system, as an effect of amendments–reamendments.

For the purpose of this study, it is considered that in long-term experiments and multi-year fertilization, calcium corrects acidity by neutralizing its active forms (Ah, mobile Al), but on reamendment and over-amendment, it disrupts the regime of other cations in CEC, of Mg and K especially [21–24].

Therefore, balanced fertilization maintains a controllable Ca/Mg and Ca/K ratio and normal fertilization with NPK management ordering calcium functions [25,26].

Magnesium chemism may, in long-term experiments and multi-year fertilization, lead to the occurrence of processes requiring Mg agrochemical control:

- With pH reduction, acidification and acidity correction (by $CaCO_3$, without $CaCO_3$ and $MgCO_3$) update interferences with Ca^{2+} and with Al^{3+}.
- With the promotion of potassium in differentiated NPK systems, there is subsequent interference with K^+ alongside frequent deficiency states [27–29].

Previous observations on the chemistry of the S, Ca, and Mg elements have led to the present soil investigation and monitoring, through long-term experiments, towards the observation of their fertility changes, determined over several years, and aiming at the formulation of proposals for prevention or remediation through agrochemical measures, amendments (in acidic soils), and balanced fertilization [12].

The application of S, Ca, and Mg has not yet become a widespread practice in Romanian agriculture, but it is still related to changes in fertilization systems and implicitly in their monitoring indicators. Thus, S application is considered for this study as a function of its efficiency as an accompanying anion (SO_4^{2-}) but also in enhancing N efficiency. The deepening of the chemistry and effects of Ca-Mg has been extended in the present approach, especially to the effects of amending acidic soils [28,29].

In this context, this paper approaches the substantiated correct application of the elements mentioned, which is highly required, and its effects, especially in the context of long-term, stationary fertilization approaches, in areas where S, Ca, and Mg fertilization has been excluded.

2. Materials and Methods

In order to achieve the proposed research objectives, namely determining the chemistry of the S, Ca, and Mg elements in the soil-plant system and then the conditions of opportunity and effect of their application, the following experiments and analyses were undertaken:

1. An amendment ($CaCO_3$) experiment was carried out to study Ca-Mg-K interaction.

Lime doses from Ah (hydrolytic acidity):

- 0 Ah; 0.5 Ah; 1.0 Ah; 2.0 Ah;

- Fertilizer background: $N_{100}P_{70}K_{60}$;
- Grain maize crop.

This experiment with increasing doses of $CaCO_3$ was conducted on an amendable, albic luvisol, in order to study the comparative effect of $CaCO_3$-based amendments in relation to the modification of Mg chemistry in this soil, which had been dealkalized, and to evaluate the possibility of using and extending the application of dolomitic limestones (which can favorably regulate this Ca/Mg ratio and physico-chemically balance the new soil).

2. Long-term experiments [30,31] at the Office of Pedological and Agrochemical Studies Alba (OSPA Alba) and the Turda Agricultural Research and Development Station (SCDA Turda) (for 55 years of fertilizing effect, during the 1967–2022 period), with exclusively mineral NP fertilizations, have endangered the S status and chemistry, previously predicted as exposed to a reduction in the humus reserve of the investigated soils over time. The reduction in this indicator may reveal the need for its application from NP mineral compositions, NP + S + Mg, or from organic input (in organo-mineral fertilizations). The evolution of total S and mobile content was monitored in the following long-term NP experiments at OSPA Alba and SCDA Turda:
    - NP experiments: 0, 40, 80, 120, 160 kg N a.s./ha, wheat;

    0, 50, 100, 150, 200 kg N active ingredient/ha, maize;
    0, 40, 80, 120, 160 kg P_2O_5 active ingredient/ha, wheat and maize;

- Soil: wheat, maize, soya.

3. The effect of S + Mg application (from $MgSO_4$) on wheat, maize and soybean (5-year average) was monitored as follows:
    - Promotion of S, Ca, Mg fertilization with various simple and complex assortments on various crops.

In the context of Romanian agriculture, these experiments evaluated the possibilities of using some mineral products available on the fertilizer market in compositions usually including either NPK + Kiserit or conventional manure + NPK.

4. The soil characteristics in the experiments conducted were as follows:

    4.1. Alluvial mollisol:
    Located in the floodplain of the Mures river, at the basis of its terrace;

— Pedological characteristics: protic soil class, Am diagnosis horizon;
— Agrochemical characteristics: pH 7.2–7.4 (weak alkaline); humus—2.60–2.90% (medium supply); 10–15 ppm P (medium supply); 150–170 ppm K (good supply).

    4.2. Typical preluvisol:
    Located in the upper floodplain of the river Mures;

— Pedological characteristics: luvisol class, superficial A0 horizon and Bt intermediate one;
— Agrochemical characteristics: pH 5.6–5.8 (moderately acidic) borderline amendable; V—80–85%; humus—2.20% (low-medium supply); I_N = 1.72; 5–6.5 ppm P (very low supply); 120–130 ppm K (medium supply).

    4.3. Albic luvisol:
    Located in the Somes-Tur plain;

— Pedological characteristics: luvisol class, superficial Ap-Ea-BEw horizon;
— Agrochemical characteristics: pH—4.8–5.2; V—38–42%; humus—1.4%; P-AL—8–10 ppm (low supply); 130–140 ppm k (medium supply).

    4.4. Chernozem–phaeozem:

— Pedological characteristics: in the current taxonomies, vertic clay–loam chernozem or vertic clay–phaeozem;
— Agrochemical characteristics: pH—6.90–7.10; T—59.14 m.e.; V—96%; humus—3.92; Nt—0.196%; P—15 ppm; K—250 ppm.

5. Current agrochemical analyses performed (method):

- pH_{H2O}, potentiometric; titrimetric Ah; mobile Al [32]; exchangeable Ca and exchangeable Mg spectrophotometry in ammonium acetate extract [33–35]; exchangeable (mobile) K in ammonium acetate–lactate (AL) solutions [36].

Analysis of variance (ANOVA) was performed on the yield, using the Polifact statistical software to identify the significant differences between yields.

6. Interpretation limits of S, Ca, and Mg chemistry for soil analyses [5,33].

The interpretation of analytical data of the soil supply state and specific and global nutrient consumption of crops was performed considering literature data synthesized in the following Tables 1 and 2.

Table 1. Optimum average contents of nutrients in soil (limits of interpretation) (taken from various authors, [5]).

Item	Indicator	Supply		
		Insufficient	Optimal	Excess
Sulfur S, SO_4^{2-}	IAS *	<9	10–19	>19
	$S\text{-}SO_4$, ppm (Method 1, 2)	<5	5.1–10	>10
	Loss S:	<10	10.1–50	>50
	IAS	<5		
	$S\text{-}SO_4$, ppm	<3		
Calcium Ca^{2+}	Exchangeable calcium from % (TY *)	<35	35–70	>70
	Soluble calcium, ppm	<100	100–150	>500
	Deficiency Ca:			
	Ca, % of T	<20–30		
	Soluble Ca, ppm	<50–70		
Magnesium Mg^{2+}	Exchangeable Mg, % of T	<2	2–8	>8
	Soluble Mg, ppm	<60	60–500	>500
	Water-soluble Mg, ppm	<3	3–6	>6
	Mg deficiency:			
	Mg, % of T	<6		
	ICMg = Exchangeable Mg/Ksch.FR ***	0.3	0.30–0.60	>0.60

*** T—cation exchange capacity (CEC); * IAS—sulfur supply index; IAS = (%humus × %S) × 100.

Table 2. Specific intakes (Cs = kg/t) of fertilizer elements in some crops [5] (genotypes grown in Romania).

Crop	Fertilizing Elements Cs/kg/t					
	N	P_2O_5	K_2O	CaO	MgO	Soluble S
Wheat-autumn	29	16	29	8	4	2
Grain maize	28	18	30	12	4	3
Rapeseed	55	40	50	50	25	25
Sunflower	50	30	60	35	20	12
Soya	75 *	30	40	25	15	12
Sugar beet	6	4	8	4	3	2
Potatoes	7	4	9	4	3	3

* Sixty to seventy percent by symbiotic fixation.

3. Results and Discussion

The application of fertilizers in long-term experiments and multi-annual fertilization determine essential changes in soil fertility leading to highly diversified soil-plant environments, which are strongly reflected in the evolution of fertility in the medium and long term, thus having proven effects on soil productivity [22,24,36].

In this context, the experiments at OSPA Alba and SCDA Turda, with the results summarized above, reveal essential changes in pH, organic C, and humus content as well as in the level of nutrient representation. The newly created conditions determine particular and differentiated agrochemical states, influential in making decisions related to soil protection and modeling factors for the existing fertility and environmental conditions.

1. Results from the study of Ca-Mg-K interaction under conditions of amendment and fertilization of acidic soils:

The acidification of soils over long-term NP and NPK fertilization, where nitrogen is the determining factor, especially in excess or disproportionate doses, raises particular management issues for preventing nitrogen overdosage but also correcting the reaction [21,37,38].

Amendment and reamendment on acidic soils in need of acidity neutralization (with pH_{H2O} < 5.8; V < 75% and mobile Al > 0.3 m.e./100 g soil) with materials containing exclusively $CaCO_3$ mainly cause an increase in the level of base saturation of the adsorbent complex, primarily at the expense of Ca^{2+} ions and at the expense of Mg^{2+} ions, with a reduction in their representation in the cation exchange capacity (<% Mg^{2+} of CEC or T). This essential modification is reproduced at the tissue level, obviously to the detriment of the Mg regime in the context of Ca/Mg interaction. It ultimately leads to a prognosis of nutrient insufficiency. Additionally, the remediation of acidic soils negatively accentuates this interaction (Table 3).

Table 3. Changes in Ca and Mg content of soils and plants under the influence of lime amendment. Crop: maize; soil: albic luvisol.

Liming Level Ah	Soil Analysis			Plant Analysis				Ca/Mg Ratio
	pH_{H2O}	Exchangeable Ca n.e.	Exchangeable Mg m.e.	Ca% Stems and Leaves	Mg % Stems + Leaves	Mg % Roots	Mg % Ratio 1/2	
0 Ah $CaCO_3$	4.18	1.2	0.90	0.28	0.27	0.21	1.3	y = 0.28 − 0.16x r = −0.800 (Gl-16)
0.5 Ah $CaCO_3$	5.50	4.8	0.63	0.52	0.18	2.96	2.9	
1.0 Ah $CaCO_3$	6.36	7.9	0.53	0.69	0.17	1.76	4.9	
2.0 Ah $CaCO_3$	7.21	11.9	0.30	1.60	0.12	0.71	13.3	
1.0 Ah $CaCO_3 \cdot MgCO_3$	6.58	5.8	1.09	0.58	0.38	1.34	1.5	-

By comparison to acidity neutralization achieved with $CaCO_3$ (exclusively), the alternative of correcting the acid reaction with dolomite ($CaCO_3$-$MgCO_3$) and with an initial content of 20–24% MgO sufficiently controls the Ca/Mg ratio in the soil and plant. Moreover, the agrochemical regime of the elements involved diminishes the predominant effect of Ca^{2+} in the cation exchange capacity. The priority of using dolomite as an amendment for acidic soils is determined in correcting these soils' reaction where Mg representation is deficient and is contained in a dissolvable form (Mg soluble in HCl 0.05 N) in amounts less than 1 m.e./100 g soil and in a soluble state (Mg in Ac-NH_4) in concentrations less than 50–100 ppm [15,17].

The correction of the acid reaction of soils is enhanced in effect by complex fertilization measures that mutually support each other's role and effects, proving sustainable and positive for the improvement of acidic soils and soil fertility protection. In this context, fertilization accompanying amendment realigns the interactions of the nutrient ions involved and imposes remodeling in the structure of cations and fertility indicators. Thus, NPK application with the presence of K at doses and levels differentiated according to soil and crop consumption updates the K/Mg interrelationship while also determining a decrease in Mg representation in its exchangeable and soluble forms in the presence of amendments (Table 4).

Table 4. Magnesium and potassium chemistry in amended albic luvisol; crop: maize; soil: albic luvisol.

Ah Amendment Level	Mg-ppm		Report 1/2	K-ppm		4/5 Ratio
	in HCl-0.05 N	in Ac-NH_4		Unexchangeable	Exchangeable	
$CaCO_3$	1	2	3	4	5	
0 Ah $CaCO_3$	336	108	3.1	614	83	7.4
0.5 Ah $CaCO_3$	300	76	3.9	637	30	11.3
1.0 Ah $CaCO_3$	288	64	4.5	657	66	9.9
2.0 Ah $CaCO_3$	252	36	7.0	734	97	7.6
1.0 Ah $CaCO_3 \cdot MgCO_3$	428	144	2.9	582	124	4.2

The one-sided nature of the amendment (only with $CaCO_3$-based neutralizing materials) enhances Ca/K and Ca/Mg antagonism. It even ensures an increase in the concentration of the unexchangeable forms with K cations participating as part of exchange-free fixation processes in the interlamellar spaces of clay minerals (here, illitic), with increased absorption energy. However, the application of limestone amendments with Ca + Mg dolomite ($CaCO_3$-$MgCO_3$) attenuates the negative and depressive K/Mg interrelationship. Also, in the context of the cation exchange capacity, the other cationic relations Ca/K, Ca/Mg, and K/Mg are concomitantly controlled, simply shaping the regime of these essential elements, increasing and redistributing their presence between the forms held in relation to the adsorptive complex. These processes, with the improvement of the composition in the cation exchange capacity, reaching a desired equilibrium should be promoted as a measure to protect and develop soil fertility and prevent nutrient impact or imbalances [39–41].

In agricultural soils that do not require the application of amendments, the content modeling for particular exchangeable cations and nutrients, primarily in the case of crops with specific consumption (Cs = kg/t) of N, P, K, Ca, Mg, and S, is carried out by complex fertilization (Table 5.)

Table 5. Effect of NP, NPK + S complex fertilization on sunflower; soil: alluvial mollisol; long-term stationary; OSPA Alba (20 years).

Total Fertilization kg Active Ingredient/ha	Basic Fertilization kg Commercial Substance/ha Active Ingredient/ha	Phase Fertilization kg Commercial Substance/ha Active Ingredient/ha	Production kg/ha	Average Production (Grain) kg/ha	Sigificance of Difference
$N_{140}P_{80}K_0$	400/20-20-0 80-80-0	180/AN; 60 N 130/h; 60 N 220/CAN; 60 N	4540 4520 4580	4547	ns
$N_{140}P_{80}K_{80}$ + 70S	533/15-15-15-12.8S 80-80-80 + 70S	180/AN; 60 N 130/h; 60 N 220/CAN; 60 N	4620 4530 4660	4603	**
$N_{140}P_{100}K_{100}$ + 70S	533/15-15-15-12.8S 80-80-80 + 70S	260/23-9-9 + 0.5CaO + 0.5MgO + 0.05Zn + 0.05B 60-23-23-Mg + Ca + Zn + B	4820	4820	**
$N_{140}P_{80}K_{80}$ + 70S	533/15-15-15-12.8S 80-80-80 + 70S	220/CAN; 60 N + Ca + Mg	4700	4700	**

Legend: ns—no significant differences; ** distinct significant differences.

The fertilizer resources applied (involving yields and treatments over a period of 5 years, in a stationary system) included the following variants: AN (with 33.5% N); urea (with 46%N); CAN (with 27%N + min. 7% CaO; min. 5% MgO); NPK complex (15-15-15 + 12.8S); NP complex (20-20-0); NPK + Ca + Mg complex (23-9-9 + CaO + MgO).

Soil agrochemical monitoring shows a steady reaction state (pH), with minimal changes (+ΔpH) when applying CAN variants and the maintenance of agrochemical indicators with normal (optimum) contents [21,22,29,31].

The data showing the effect of complex fertilization in sunflowers reveals that a plant with such a high nutrient consumption, even considered a rapacious one, significantly exploits the interactions between essential elements while a complementarity of the complex presence of nutrients is noticed.

2. Monitoring of total and mobile S content in long-term experiments:

According to the previous formulations and observations, it is estimated that in the humus formula, the organogenic elements can be expressed globally in the following average proportions [42]:

- Proportion of elements: C14:N1:P0.1:S0.055:H11.4:O57;
- Gravimetric ratios—elemental: 168pC:14pN:3.1pP:1.75pS:11,4pH:91.2pO;
- Percentage weights of the elements: 58%C:4.84%N:1.07%P:0.60%S:3.94%H:31.55%O.

In this complex composition of humus, S is in a reduced state as thiol groups, in sulfur-containing amino acids and heterocycles; together with the other organogenic elements, it follows the overall humus changes. Thus, several expressions are known, showing a total dependence of the total S content on the total C content in soils. The changes that occur in humus evolution (organic C) in long-term experiments—a decrease, a constant, or an increase in terms of the humus content—are also evident in total and mineral S [24,30,36].

- Long-term NP and organo-mineral experiments at OSPA Alba

The analytical data presented above showed several "patterns" of humus (organic) dynamics with values showing their constancy in the typical preluvisol upon NP fertilization and significant changes in the fertilized and amended variants, as well as in those that benefited from more active conventional tillage (in row crops and maize) (Tables 6–8).

Table 6. Dynamic changes in humus—organic C content in typical preluvisol under wheat cultivation.

Unamended				Amended			
Fertilization Variant	**Humus %**	**Fertilization Variant**	**Humus %**	**Fertilization Variant**	**Humus %**	**Fertilization Variant**	**Humus %**
P_0N_0	2.30	$P_{80}N_0$	2.18	P_0N_0	2.40	$P_{80}N_0$	2.27
P_0N_{40}	2.23	$P_{80}N_{40}$	2.30	P_0N_{40}	2.29	$P_{80}N_{40}$	2.24
P_0N_{80}	2.27	$P_{80}N_{80}$	2.34	P_0N_{80}	2.34	$P_{80}N_{80}$	2.31
P_0N_{120}	2.32	$P_{80}N_{120}$	2.28	P_0N_{120}	2.31	$P_{80}N_{120}$	2.16
P_0N_{160}	2.34	$P_{80}N_{160}$	2.34	P_0N_{160}	2.37	$P_{80}N_{160}$	2.29
Media	2.29	-	2.62	-	2.34	-	2.25

Table 7. Dynamic changes in humus—organic C content in typical preluvisol under maize cultivation.

Unamended				Amended			
Fertilization Variant	**Humus %**	**Fertilization Variant**	**Humus %**	**Fertilization Variant**	**Humus %**	**Fertilization Variant**	**Humus %**
P_0N_0	2.10	$P_{80}N_0$	2.15	P_0N_0	2.14	$P_{80}N_0$	2.26
P_0N_{50}	2.10	$P_{80}N_{50}$	1.75	P_0N_{50}	2.15	$P_{80}N_{50}$	2.06
P_0N_{100}	1.89	$P_{80}N_{100}$	2.18	P_0N_{100}	2.11	$P_{80}N_{100}$	2.07
P_0N_{150}	2.00	$P_{80}N_{150}$	2.03	P_0N_{150}	2.00	$P_{80}N_{150}$	2.08
P_0N_{200}	2.13	$P_{80}N_{200}$	1.86	P_0N_{200}	1.98	$P_{80}N_{200}$	1.88
Media	2.04	-	1.99	-	2.07	-	1.88

Table 8. Dynamic changes in humus—organic C content in alluvial mollisol cultivated with wheat and maize.

Alluvial Mollisol—Wheat				Alluvial Mollisol—Maize			
Fertilization Variant	**Humus %**	**Fertilization Variant**	**Humus %**	**Fertilization Variant**	**Humus %**	**Fertilization Variant**	**Humus %**
P_0N_0	2.64	$P_{80}N_0$	2.70	P_0N_0	2.45	$P_{80}N_0$	2.64
P_0N_{40}	2.65	$P_{80}N_{40}$	2.76	P_0N_{50}	2.70	$P_{80}N_{50}$	2.65
P_0N_{80}	2.68	$P_{80}N_{80}$	2.90	P_0N_{100}	2.71	$P_{80}N_{100}$	2.75
P_0N_{120}	2.72	$P_{80}N_{120}$	2.91	P_0N_{150}	2.65	$P_{80}N_{150}$	2.66
P_0N_{160}	2.65	$P_{80}N_{160}$	2.70	P_0N_{200}	2.60	$P_{80}N_{200}$	2.57
Media	2.67	-	2.79	-	2.62	-	2.65

First and foremost, the results presented show that in acidic, amendable, typical preluvisol, with pH 5.7–5.8, V% 75–78, and mobile Al 0.2–0.3–0.4 m.e./100 g soil by amendment, for four cycles (at 5 years $CaCO_3$ was applied after Ah), there is a substantial reduction in the humus (and organic C) [37] content, more significantly under maize cultivation (as this crop benefits from conventional tillage). Contrary to this phenomenon, due to amendment but also to tillage, in alluvial mollisol (with pH 7.2, humus content 2.6–2.7%, saturated type), the dynamic process of humus content change reveals that the saturation in bases and better soil buffering capacity lead to stability in the soil-plant system and even to positive effects on the humus content. In these instances, at high humus content, the water-soluble humus fractions continuously feed the carbon cycle and maintain the permanent dynamics of the humic components. Moreover, in these cases, relative stability is maintained, and a positive result is observed in the case of soybean as a preplant for wheat. In maize, soil tillage mitigates some positive phenomena in humus dynamics (they may become slower and show better mineralization).

In the context of these phenomena and knowledge of N/S dependencies (in the soil, primarily between organic formations) the evolution of total S and mobile forms of S can be properly studied (Table 9).

Table 9. Evolution of S forms in different soils, fertilized multi-annually (20 years).

Crop/Soil/Amendment	Fertilization Variant	Humus %	Organic C %	Total S %	IAS *	$S\text{-}SO_4$ ppm
No amendment wheat/typical preluvisol	$P_0N_{0–160}$	2.29	1.33	0.020	4.5	4/<5
	$P_{80}N_{0–160}$	2.28	1.32	0.021	4.8	4/<5
Amendment wheat/typical preluvisol	$P_0N_{0–160}$	2.34	1.35	0.021	3.7	4/<5
	$P_{80}N_{0–160}$	2.25	1.31	0.020	3.6	3/<5
No amendment maize/typical preluvisol	$P_0N_{0–160}$	2.04	1.18	0.018	3.3	3/<5
	$P_{80}N_{0–160}$	1.99	1.15	0.017	2.1	3/<5
Amendment maize/typical preluvisol	$P_0N_{0–160}$	2.07	1.20	0.019	3.3	3/<5
	$P_{80}N_{0–160}$	1.88	1.09	0.017	3.0	3/<5
wheat/preluvisol alluvial mollisol	$P_0N_{0–160}$	2.67	1.55	0.027	7.2	5/7–10
	$P_{80}N_{0–160}$	2.79	1.62	0.029	8.1	5/7–10
maize/preluvisol alluvial mollisol	$P_0N_{0–160}$	2.62	1.52	0.027	7.1	4/6–7
	$P_{80}N_{0–160}$	2.67	1.55	0.027	7.2	4/6–7

* S supply index (IAS) = (%Humus × %S) × 100.

In all the analytical control alternatives, the S-l representation in the two soils—preluvisol and alluvial mollisol—is in a poor concentration in the acidic soil and borderline insufficient/sufficient in the alluvial mollisol. Evidently, the representation and evolution of this element correlate with organic C concentrations and changes and, thus, with humus.

- Long-term experiments at SCDA Turda

Analytical data from the long-term experiment, located at SCDA Turda on a chernozem–phaeozem, with high productive potential, specific to the Transylvanian Plain, show differences in the evolution of humus and implicitly in the evolution of S reserves.

Agrochemical monitoring conducted over the 1969–2020 period generally shows reductions in humus (and organic C) content in both the unfertilized (where the decrease is more significant) and fertilized variants (Table 10).

Table 10. Humus (%) and sulfur (IAS) content with long-term application of NP fertilization (1966–2020); soil: silty clay loam—vertic.

Indicator Tracked	NP Fertilization	Years/% Humus—% of Original									Difference from the Original
		1968	1984		1995		1999		2020		
Humus	N_0P_0	3.78	3.90	103	3.21	84	3.18	84	3.12	82	−0.66%
	$N_{120}P_0$	3.72	3.50	94	3.37	91	3.26	88	3.21	86	−0.51%
	$N_{120}P_{120}$	3.68	3.83	104	3.47	94	3.31	88	3.19	86	−0.49%
IAS	N_0P_0	13.1	13.7		11.2		11.1		10.9		−2.20
	$N_{120}P_{120}$	12.9	13.4		12.1		11.5		11.1		−1.18

The clay–loam chernozem with a neutral reaction state (pH), high clay content (50–52% clay), and good humus supply (>3.50%) has a relevant buffering capacity (well represented T and CEC, humus + clay at a high level). In the 52 experimental years with NP fertilization adapted to a 3–5-year crop rotation, the humus content was reduced in the unfertilized variant by 0.66% and in the fertilized variant by 0.49–0.51% after 52 years, the reduction being diminished in the complex $N_{120}P_{120}$-fertilized variant. The S content, characterized by the "supply index" (IAS = %Humus − %S − 100), decreased by more than one unit in the fertilized variants and by more than two units in the non-fertilized alternative.

Under these conditions (with the three different soils—preluvisol, alluvial mollisol, chernozem), resulting from the reduction in humus (and organic C) content, sulfur being the organogenic element of humus, the application of S resources (here $MgSO_4$) has been experimented with in order to study the effect conditions on wheat-maize-soybean production and changes in soil content as an effect of this technology [38] (Table 11).

Table 11. Effect of $MgSO_4$ application on wheat, maize, and soybean yield (60 kg S-SO_4/ha); soil: alluvial mollisol.

Fertilization Variant *	Prod. kg/ha	Diff. kg/ha	Significance of the Difference	Prod. kg/ha	Diff. kg/ha	Significance of the Difference	Prod. kg/ha	Diff. kg/ha	Significance of the Difference
		Wheat			Maize			Soya	
Control C_1	3056	-	-	6591	-	-	2253	-	-
NPK-DOE C_2	4699	1643 -	***	8172	1581 -	***	2454	201 -	***
NPK-DOE + Mg + S	4877	1821 178	***	8883	2292 751	***	2853	600 399	***
NPK-DOT	4765	1709 66	***	8694	2103 522	***	2894	641 440	***
NPK-DOT + Mg + S	4885	1799 186	***	8904	2313 732	***	2979	726 525	***
F.O.-1/3-DOE + NPK ind. DOE	4664	1608 −35	***	7913	1322−259	**	2627	374 173	**
F.O.-1/3-DOE + NPK ind. DOE + Mg + S	4861	1805 162	***	8210	1619 38	***	2906	653 152	***
F.O.-1/3-DOT + NPK ind. DOT	4854	1798 155	***	8774	2183 602	***	3106	853 471	***
F.O.-1/3-DOT + NPK ind. DOT + Mg + S	4954	1898 255	***	8914	2323 712	***	3246	993 792	***
DL $_{C1}$		476 (5%) 641 (1%) 849 (0.1%)		DL $_{C1}$	787 (5%) 1058 (1%) 1401 (0.1%)		DL $_{C1}$	238 (5%) 319 (1%) 423 (0.1%)	

Legend: -, no difference; * significant differences; ** distinct significant differences; *** very significant differences. DOE—best economic dose; DOT—best technical dose; F.O.-1/3 of DOE and DOT.

It can be assessed from the experimental results obtained that in a soil with low to medium supply of S and Mg, with a long-term reduction (in experimental stationary variants) in S content, concomitant with organic C and humus, the application of S + Mg fertilizer resources (with Mg + S), on an NPK or organo-mineral background, leads to yield increases in the three crops—wheat, maize, and soybean. The effect becomes determined with increasing soil fertilization levels using NPK and organo-mineral fertilization, even in complex fertilizer structures and components. There are previous data supporting the effect of S and Mg determined mainly by N- (or other elements, starting with their accumulation in roots, prior to their accumulation in leaves) [3–5,40–45].

In this framework of the S + Mg effect, a triggering factor of the phenomenon may also be the initial low representation of S (<0.0017% in total forms or <3.0% IAS and even <10 mg kg^{-1} mobile S) and Mg < 10 mg. These states may determine the need for fertilizer application with these elements (the initial supply of S and Mg elements to soils may also be related to their interactions and to K application and representation in soils or fertilizer formulations) [39].

In S-cation (K, Mg, etc.) interrelationships, the role of the S anion (SO_4^{2-}) as a companion anion to these elements is reconsidered alongside the activation effects and roles of cations in general, compared to S and Mg roles in photosynthesis and proteosynthesis [46].

The effect of S + Mg is more pronounced and significant, even in relation to the N and K nutrients, in the form of fertilizing applications of these complexes in diversified assortments [13] (Table 11).

- Promotion of S, Ca, Mg fertilization with various simple and complex assortments on various crops.

Complex and multi-element fertilizations are proven requirements for most genotypes. In the context of fertilizer application technologies, they are becoming alternative applications and aid in the development of sustainable agricultural systems. They exploit the multiple-factor interactions and elements involved, prevent negative nutrient conditions, and ensure the stability and even development of current and multi-annual soil productivity and fertility [47] (Table 12).

Table 12. Efficient promotion of NPK+ fertilizer varieties (with S and Kiserit) in rapeseed. Soil-chernosem; pH—6.9–7.1; average lot yield = kg/ha.

Total Fertilization kg a.s./ha	Autumn Commercial Substance/ha	Spring Commercial Substance/ha	Yield kg/ha	Diff. kg/ha	Significance of Difference
Control $N^{120}P^{80}K^{80}$	300/16-16-16 (MOP) 60-60-60	60-0-0 AN	3680	-	
$N^{120}P^{80}K^{80}$ + 50 S (K_2SO_4)	400/NPK 15-15-15 +SO_4 60-60-60	60-0-0 AN	4275	495	ns
		60-0-0 Urea	4212	532	*
		60-0-0 CAN	4166	486	-
$N^{120}P^{80}K^{80}$ + 30S + 17MgO	428/NPK+ (14-14-14 + 7S + 4MgO) (from kiserit) 60-60-60	60-0-0 AN	4348	668	**
		60-0-0 Urea	4366	686	**
		60-0-0 CAN	4280	600	*
$N^{120}P^{80}K^{80}$ + 30S + 17MgO + CaO + MgO + B + Zn	428/NPK+ (14-14-14 + 7S + 4MgO) (from kiserit) 60-60-60	60-23-23 + 0.5CaO + 0.5MgO + 0.05B + 0.05Zn 23-9-9 + CaO+ MgO + B + Zn	4489	809	***

Legend: -, no difference; ns—no significant differences; * significant differences; ** distinct significant differences; *** very significant differences.

These complex fertilizations can be part of sustainable fertilization systems with economic effects in the soil-plant system that ensure the balance and protection of consumer nutrition, fertility stability, and productivity. These systems are proving directly useful and current, in the context where all platforms of long-term experiments have proven the necessity for real management of fertilizer use and supported medium- and long-term modeling of basic soil indicators—of chemical, nutrition, physical, and biological ones.

The long-term application of fertilizers in stationary systems leads to essential, dynamic changes in the determinants of fertility. In the determinations presented in the current paper, the major changes affect the long-term state of soil reaction through a differentiated supply of ions involved in nutrition. These changes also lead to other modifications in substance reserves in the organic soil component and create a differentiated regime in the soil supply for the main fertilizing elements resulting from the applied fertilizer varieties. This leads to positive and negative realignments and patterns in the soil-plant system, which are constantly subject to the dynamics caused by technological anthropic pressures.

4. Conclusions

In this context, it was shown that the application of fertilizing resources containing S, Ca, and Mg can represent prevention and modeling measures for some essential fertility indicators and thus contribute to nutrition management.

The experimental data presented herein reveal that sulfur application becomes topical as its organic form is reduced (concomitant with organic C and humus in the soil) if fertilization is performed within NP or NPK systems, as essential nutrient ratios favor nitrogen. In this context of N/S ratio modeling, the valorization of the particular and complementary effect of nitrogen leads to control and support for sulfur application. As an accompanying anion (SO_4^{2-}), it contributes to the modeling and effect of essential cations (Ca^{2+}, Mg^{2+}, K^+).

It has also been shown that calcium (an essential cation in the soil and in the plant) requires control and modeling, both in principle and in practice, upon amendment and reamendment of acidic soils, where the application of dolomitic limestone ($CaCO_3$-$MgCO_3$) supports the Ca/Mg ratio and prevents interference with representative ions.

Magnesium application and modeling, through complex combinations, favor essential cation interaction (Ca, Mg, K), while such fertilizer systems as NPK + S + Mg also favor this model of complex fertilization (a distinct measure compared to Mg interventions in the melioration of acidic soils).

Therefore, the interaction observed in this study between S, Ca, and Mg and the primary chemical elements employed in agriculture (NPK), relevant for multi-annual stationary fertilization, is practical and efficient in such contexts as the application of sustainable fertilizing technologies. From this point of view, further research is recommended in fertility monitoring with amelioratory and protective measures on a sustainable basis.

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